# Laboratory Directions

IN

# Chemistry I-A

EDITED BY

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IN THE

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CHEMISTRY 1A. UNIVERSITY OF CALIFORNIA

# LABORATORY DIRECTIONS, 1915

Provide yourself with a notebook about 8 inches by 5 inches in size and not loose-leaved.

Notes about recording the results of experiments are given in the first three assignments and these notes apply to all later assignments.

Bring your lecture notes and textbook of inorganic chemistry into the laboratory and use them for reference.

Satisfactory progress can be made in this course only when the student accepts the responsibility of mastering, before the next period, the material presented in each lecture and laboratory period. Consult your instructor in the laboratory or at the quiz section about your difficulties. Frequent brief tests will be given, usually at the beginning of the period.

*At the first meeting of your laboratory section* go to the room to which you have been asigned (consult posted lists or inquire at office if necessary), apply to your instructor for your key, check your apparatus by means of the list in your locker, sign your name (surname first) in the proper place, and return this list to your instructor. Begin the first assignment.

If, while checking your apparatus during the first laboratory period, any article is found to be damaged, exchange it at the office, or sign a blue "return slip" in order that you may receive proper credit if the damaged article is broken during the term.

Fill your wash-bottle with distilled water. Sterilize the mouth-piece by placing it in boiling water for a minute or two. Always use the distilled water in your wash-bottle for the final rinsing of apparatus.

Rinse out your five reagent bottles, partially fill them with the 6 normal laboratory solutions. Note that, while pouring the reagent from one of these bottles, the stopper of the bottle should be held with the same hand that holds the test tube or beaker.

In general, avoid contamination of any of the reagents in the laboratory by keeping each stopper clean and returning it at once to the proper bottle.

Articles to replace broken apparatus, and additional articles for regular use, are obtained at the office in the corridor (on the same floor as your room) by filling out a white order slip and signing your name and desk number.

A yellow "temporary order slip" is used instead of a white order slip when borrowing articles specified in the last paragraph of the list of apparatus given below. These articles must be returned during the same laboratory period before the office is closed.

Sign a blue "return slip" whenever any article is returned to the office. The article will not be accepted unless it is clean and in good condition.

## *List of Apparatus.*

I. Regular equipment of each locker. At the end of the term the locker must contain the same amount of apparatus, no more and no less; the locker must be clean; the apparatus must be clean and dry, and in good condition; glass stoppers must fit, and be protected by the insertion of a piece of paper.

1 Key.
5 Beakers, 100 cc., 150 cc., 250 cc., 400 cc., 600 cc.
5 Reagent Bottles.
2 Sample Bottles, 50 cc.
1 Graduated Cylinder, 50 cc.
4 Flasks, 500 cc., 250 cc., and two 125 cc.
1 Wash-bottle, equipped with glass tubing and rubber stopper.

2 Funnels.
2 Blue glasses.
2 Glass Rods, 12 cm. and 18 cm.
30 cm. Glass Tubing.
12 Test-tubes.
1 Watch Glass.
1 Casserole.
1 Crucible, with cover.
2 Evaporating Dishes, 6 cm. and 9 cm.
15 cm. Rubber Tubing, 3 mm.
1 Bunsen Burner, with rubber tubing.
1 Wire Gauze.
1 Triangle.
1 Test-tube Brush.
1 Test-tube Holder.
1 Test-tube Rack.
1 Package Filter Paper.
1 Rule.
2 Towels.

II. Additional articles may be obtained at the office:

(a) By signing the regular white order slips.

Special apparatus for Assignments III and V, first term.
Matches.
Glass Flasks, 50 cc.
Corks.
Rubber Stoppers.
Platinum Wire and Platinum Foil. Partial credit will be given at the end of each term for Platinum Wire and Foil returned to the office.

(b) By signing yellow temporary order slips.

Burettes, with clamps and pinchcocks.
Graduated Cylinders, 10 cc. and 250 cc.
Files.
Paraffin.

## ASSIGNMENT I.

### Measurement of Volumes.

*Notes*: Enter the date and the title of the exercise at the top of a page of the *notebook*. Use one side only of each page for recording experimental results and answering questions. Make calculations neatly at the bottom or side of the page, or on the opposite page. Show your notebook to your instructor each day until he is satisfied with your method of making entries.

Each day, before leaving the laboratory; finish the experiments assigned for the day's work, write out the answers to as many of the questions as possible, and clean the top of your desk.

Before the next laboratory period finish the questions and problems, review your work and be sure that you understand it perfectly. Read over the laboratory notes on the next laboratory exercise.

*Experiment.* Make several measurements of the inside diameter (in centimeters) of your medium-sized beaker. (The instructor will suggest a method.) Record each measurement in your notebook as soon as it is made. The beakers are not perfectly cylindrical, nor is the method very accurate; the measurements, therefore, will usually show variations of a few tenths of a centimeter. An average of at least four measurements will give the mean diameter to about 0.1 cm. *Questions*: What fraction of the diameter is this error? What percent of the diameter is this error?

*Experiment.* Fill the beaker with water to just below the flare. Measure

the depth of the water by dipping the rule into the beaker. Repeat the measurement. Mark the level of the water by pasting a piece of gummed paper on the outside of the beaker. Do not pour the water out of the beaker.

Calculate the area of the cross section of the beaker from your average value of the diameter (assume $pi = 3.14$). From this result and the depth of the water, calculate the volume of the water in the beaker.

Make further calculations to determine (1) what the change in the area of the cross section of the beaker would have been (in sq. cm) if the diameter had been 0.1 cm. greater than the value chosen; and (2) what the change in the calculated volume (in cc.) would have been if the depth of the water had also been 0.1 cm. greater. *Questions*: What percentage error in the area of the cross section results from an error of 0.1 cm. in the diameter? What percentage error in the volume results from errors of 0.1 cm. in the diameter and 0.1 in the depth? How many decimal places should be used in expressing the final result for the volume?

*Experiment.* Measure the volume of water in the beaker used in the previous experiment by means of a measuring cylinder graduated in cc.

Compare this measured volume with the volume calculated. If the difference is greater than the estimated error, repeat the calculations and study the following discussion to determine the reason. Repeat the measurements if necessary.

*Note.* If you discover an error in your previous work, do not erase your first entry, nor tear out the page. Mark the rejected result and insert the correction near the original entry.

Note that the central surface of the water in a large beaker is level. Show in a drawing the appearance of a vertical section of the surface of the water (1) where it touches the glass in the large beaker, and (2) in a small glass tube. How great is the difference (in cc.) between the readings at the top and the bottom of the *meniscus* in your measuring cylinder? Volume readings for water in glass vessels are made at the bottom of the *meniscus*.

Compare your notebook with the following sample page. Note whether you have arranged your notes neatly and systematically.

Measurement of Volumes. Aug. . . . . 1915

Used 3rd largest beaker.

| | | | |
|---|---|---|---|
| Diameter, | 6.3 cm. | Depth of water, | 7.2 cm. |
| | 6.4 " | | 7.3 " |
| | 6.3 " | | 7.2 " |
| | 6.2 " | | |
| | ——— | | ——— |
| | | Average, | 7.2 " |
| Average, | 6.3 " | | |

0.1 is 0.1/6.3 = 0.016 of the diameter. This is........% of the diameter.

| | |
|---|---|
| Area of cross section (dia. 6.3 cm.) | = 31.2 sq cm. |
| Volume calculated (depth 7.2 cm.) | = 225 cc. |
| Area calculated (dia. 6.4 cm.) | = 32.2 sq. cm. |
| Difference, | = 1.0 sq. cm. i. e.........%of the area. |
| Volume calculated (dia. 6.4 cm, depth 7.3 cm.) | = ........ cc. |
| Difference, | = ........ cc., i. e.........% of the volume. |
| Volume measured with graduate | = 219 cc. |
| Difference, | = 6 cc. less. |

This result is (or is not?) within the experimental error.

*Experiments.* Measure by means of a measuring cylinder the volumes



Barometric pressure 75.1

of a second beaker, a test-tube, and a flask. As an exercise in judging volumes, estimate the volume of another beaker and then measure it. Record in a table the volumes of your flasks and beakers. What is the volume in liters of your largest flask?

*Experiments.* Pour 10 cc. of water into a small test tube. Mark the height of the water by pasting a small label on the side of the tube. Graduate this test tube in the same way for 5 cc. and 2 cc., and set it aside for use in future experiments. Graduate your smallest beaker for volumes of 50 cc. and 100 cc. in the same way.

The paper labels on the reagent bottles in the laboratory are covered with paraffin. *Why?* Apply to the instructor to have the labels on your graduated test tube and beaker paraffined in a similar manner.

State how you would use your graduated cylinder to measure out 75 grams of water.

*Experiment,* to give practice in weighing. Weigh to 0.1 g. the small beaker which you have graduated. (See Notes on Weighing at the end of Assignment). Fill the beaker to the 50 cc. mark, and weigh. What is the weight of water in the beaker? Calculate its volume from this result.

*Problems.* (Always answer the problems before the next laboratory period.)

1. How much water would you weigh out in order to have a volume of 10 cc.?

2. How much mercury should be weighed out to give a volume of 10 cc.? The density of mercury is 13.6.

3. What is the weight of a liter of air? The density of air is 0.0012 at room temperature and atmospheric pressure.

4. Mention three methods of determining the volume of water in a cylindrical beaker.

Bring a table of atomic weights (e. g. Cady, page 96) to the laboratory for use in Assignments II-V.

*Note on Weighing.* Follow carefully the directions given by the instructor. Report to him at once if the balance is out of order or if a weight is missing. Enter the results of each weighing in your notebook while the weights are on the scale-pan and check this result while you are returning the weights to their places in the box. Summarize in a table the results of the different weighings in each experiment.

## ASSIGNMENT II.

### The Synthesis of Copper Sulfide. Weight Relations in Chemical Reactions.

(Enter the date and title of this experiment on a new page.)

The purpose of this experiment is to determine the weights of copper and sulfur which unite to form a sulfide of copper, and to calculate its formula with the aid of the atomic weights of copper and sulfur.

*Experiment.* Support a *clean* porcelain crucible, with a cover, on a triangle and heat with the colorless flame of a bunsen burner to low redness. Let the crucible cool about 15 minutes, and weigh it, with the cover, to 10 milligrams. The weights and the balances are such that weighings cannot be made closer than 10 mg.

While the crucible is cooling obtain a clean piece of copper wire, weighing about 1 gram, from the shelf and weigh it to 10 mg. *Question:* If the weight of the copper is in error by 10 mg., what is the percentage error?

Place the copper in the weighted crucible and add enough powdered sul-

fur to cover the copper. Place the cover on the crucible and heat gently (with a small flame) until the sulfur ceases to burn at the edges of the cover, but do not remove the cover while the crucible is hot. Then heat more strongly until the bottom of the crucible just becomes dull red. Again allow to cool about 15 minutes and weigh.

Carefully remove the cover and note the appearance of the contents of the crucible, but do not touch the substance. If there is any free sulfur on the cover or wall of the crucible, replace the cover, heat the crucible and cover, and weigh again. In order to check the final weight, add a small quantity of sulfur and repeat the experiment. (While waiting for the crucible to cool answer the questions in the following paragraph.) At the end of the experiment remove the substance formed, break it, and note the differences between its properties and those of copper and sulfur. To check the weight of the empty crucible, clean the crucible by placing it in a porcelain dish containing a little nitric acid and warming the mixture, rinse the crucible with distilled water, heat it, let it cool, and weigh it again. By means of a table summarize and compare the results obtained in both parts of the experiment. If there is any discrepancy (beyond 10 mg.) suggest an explanation.

What does the increase in weight represent? Is any free sulfur left in the crucible? (Give the reasons for your answers.) What would the increase in weight have been if one gram-atom of copper had been used in the experiment? How does this weight compare with the atomic weight of sulfur? What, then, is the formula of the sulfide of copper which has been formed? Write the reaction which has taken place. What is the molecular weight of the substance formed?

*Problems.* 1. (a) From your experimental results alone calculate the percentage composition of the copper sulfide formed. (b) From the atomic weights of copper and sulfur and the molecular weight of the sulfide calculate the percentage composition of pure copper sulfide. Compare the results.

2. The formula of hydrogen sulfide is $H_2S$. How much sulfur will combine with 1.008 grams of hydrogen to form this compound? What weight of hydrogen sulfide will be formed?

3. What weight of iron will combine with 32.07 grams of sulfur to form ferrous sulfide, FeS? Write the reaction. What is the percentage composition of ferrous sulfide? How much ferrous sulfide would be needed to make 34.09 grams of hydrogen sulfide?

## ASSIGNMENT III.

### The Weight of a Liter of Oxygen.

(Two students work together.) (Enter the date and title of this experiment on a new page.)

When solid potassium chlorate is strongly heated it decomposes with evolution of oxygen. The purpose of this experiment is to measure the volume of a definite weight of oxygen (obtained from potassium chlorate). This may be accomplished by heating potassium chlorate in a hard-glass test-tube, and permitting the oxygen evolved to displace an amount of water equal to its own volume. The loss in weight of the potassium chlorate gives the weight of the oxygen evolved, and the volume of water displaced gives the volume of this amount of oxygen. From these data the weight of 1 liter of oxygen can be calculated.

The potassium chlorate decomposes readily, and at a much lower temperature when a small quantity of manganese dioxide is present. The hard-glass test-tube may then be replaced by a heavy-walled test-tube of ordinary easily-fusible glass; but care must be taken not to heat the latter tube to a higher temperature than is necessary for the reaction. The manganese dioxide is a "catalyzer" in this reaction, and all of it may be recovered at

the end of the experiment after the potassium chlorate has been decomposed into potassium chloride, KCl, and oxygen.

Two students working together obtain from the office a heavy-walled glass test-tube, a rubber stopper, glass tube, rubber tube, pinch cock and clamp. One student signs a white slip for "special apparatus for Assignment III", but should make sure that the other shares the expense with him if any portion of this apparatus is broken or damaged. The apparatus should be returned as soon as the experiment is finished. Each student must keep a complete record of the experiment in his notebook.

*Experiment.* Set up the apparatus according to the diagram on the blackboard and follow the directions given by the instructor. Plan a method of testing if the apparatus is air-tight, and be sure that the pressure of the air inside the tube at the beginning of the experiment is the same as the atmospheric pressure outside. Do not begin to heat the tube containing the potassium chlorate until the instructor has examined your apparatus.

Warm the heavy-walled test-tube carefully to dry it, holding its mouth lower than its end so that a drop of water may not run down the side on to the hot glass and crack the tube. Transfer at least 1 gram of powdered potassium chlorate (half the quantity contained in the small tube) to a porcelain dish and dry it by holding it high above a bunsen flame for several minutes; be careful not to heat the substance too hot. Set the chlorate aside to cool, weigh the test-tube to 0.1 gram, transfer the potassium chlorate to the test-tube, and weigh to 0.01 g. Add a small quantity of manganese dioxide (not more than 50 mg.), mix it with the chlorate by jarring the tube, remove any powder from the outside of the tube and from the inside near its mouth, and weigh the tube carefully.

Begin the experiment by opening the pinchcock on the siphon tube, and heating the tube containing the potassium chlorate very gently with a small flame. Gradually heat the tube more strongly until the chlorate melts and gas evolution begins. Then continue to heat the tube carefully and not too strongly until enough chlorate has decomposed to force over 250 cc.. to 300 cc. of water into the receiving beaker. Now discontinue the heating and allow the tube to cool to room temperature. By raising the beaker, which holds the displaced water, equalize the level of the water in the beaker and the flask, and then close the pinchcock on the siphon tube. By means of a 250 cc. graduated cylinder measure the amount of water which the oxygen has forced out of the flask. Finally weigh carefully the hard glass tube containing the partially decomposed chlorate. *Question.* Why is it necessary to cool the test-tube and to have the water in the beaker and flask at the same level before closing the pinch-cock?

Clean the test-tube by placing water in it and shaking the mixture. The manganese dioxide is difficultly soluble in water, while both potassium chlorate and potassium chloride dissolve readily. Suggest a method of recovering the manganese dioxide and of obtaining a mixture of dry potassium chloride and potassium chlorate practically free from manganese dioxide.

To make the calculations it will be necessary to know the barometric pressure at the time you perform the experiment, and the temperature of the water in the flask. The temperature of the water may be assumed to be that of the room, and the barometric pressure will be posted on the blackboard. Enter these data in your notebook before leaving the laboratory. Below is given a table of the vapor-pressure of water at different temperatures.

*Vapor Pressure of Water.*

| Temp °C. | Vapor Pressure | Temp. °C. | Vapor Pressure |
|---|---|---|---|
| 14 | 2.2 cm. mercury | 24 | 1.2 cm. mercury |
| 16 | 2.5 " " | 26 | 1.3 " " |
| 18 | 2.8 " " | 28 | 1.5 " " |
| 20 | 3.2 " " | 30 | 1.7 " " |
| 22 | 3.5 " " | 32 | 2.0 " " |

P. in & out should be same

$P = O + $ water vapor pres.

*Questions* Assuming that the levels of the water in the beaker and the flask were the same when the pinch-cock was closed, what was the total pressure of the gas in the flask? What was the *partial pressure* of the water-vapor? Of the oxygen?

Calculate the volume of the oxygen at 1 atmosphere pressure and 0° C, the density of the gas under standard conditions, and the weight of a liter of the gas. Compare your value of the density with the one given by Cady, page 23.

*Problems.* 1. From your experiment calculate the weight of one liter of oxygen at 20°C and 754 mm. pressure.

2. Under standard conditions what weight of oxygen would occupy 22.4 liters? (Use the density obtained in the experiment.) How is this number related to the atomic weight of the oxygen?

3. What weight of oxygen could be obtained from 1 gram of potassium chlorate ($KClO_3$) by completely decomposing it?

## ASSIGNMENT IV.

### The Reaction Between Zinc and Sulfuric Acid.

The purpose of Assignment IV is to determine the quantity of zinc, which, by reacting with an acid, will set free one gram atom of hydrogen. A weighed amount of zinc is allowed to react completely with excess of sulfuric acid and the hydrogen liberated is collected in such a way that its volume can be measured.

*Experiment.* Boil about 500 cc. water in your largest beaker to expel the dissolved air.

Take a piece of zinc weighing about half a gram. If necessary, clean it with sand paper. Weigh to 5 milligrams. Do not try to cut or file the zinc in order to obtain any definite weight.

Select a beaker of such size that a small funnel when placed in it can be completely covered with water. Place the weighed zinc in the beaker, place the inverted funnel over it, and pour boiled water into the beaker until the funnel is completely covered.

Pour boiled water into a quarter liter flask until the water completely fills the flask. Without waiting for the water to cool, moisten a piece of filter paper slightly larger than the mouth of the flask, cover the mouth of the flask with the paper, taking care that no bubble of air remains below the paper. Invert the flask (over an empty vessel) and lower it into the beaker in such a manner that the stem of the funnel enters the neck of the flask. If a bubble of air enters the flask repeat this operation. The apparatus now consists of a beaker containing a funnel inverted over the zinc, and a flesk filled with water and inverted over the funnel. Place this apparatus in a basin, or other vessel, to prevent the water from overflowing on the desk during the remainder of the experiment.

Pour into the water 5 cc. to 8 cc. concentrated sulfuric acid (*CAUTION**) If the action of the acid on the zinc is slow add about 5 cc. of the laboratory solution of hydrochloric acid; stir the mixture gently but be careful not to displace the zinc from below the funnel. The hydrogen evolved rises through the funnel into the flask, but should not displace all the water in the flask.

When the zinc has all dissolved (except a few dark-colored flakes of impurities of negligible weight), place the apparatus in a large basin of water and carefully remove the beaker and funnel without allowing any air to enter the inverted flask. Keep the flask in water until it has cooled to the temperature of the water. Then raise or lower the flask until the level inside and outside the

* Concentrated sulfuric acid produces dangerous burns and should not be used carelessly. The bottle must not be removed from the lead tray. Carefully pour just enough acid for your experiment into a small beaker.

flask is the same. What is now the pressure of the gas inside the flask?) While the flask is in this position cover the mouth of the flask with the palm of the hand, remove the flask from the water and invert it. While the gas is escaping test to prove that it is hydrogen.

Fill the flask by means of a graduated cylinder, noting the volume of water needed to take the place of the gas which has escaped. Record in your notebook the barometric pressure (written on the blackboard) and the temperature of the water in which the flask was immersed.

You now have the weight of zinc taken, and the volume, at a definite temperature and pressure, of a corresponding amount of hydrogen saturated with water vapor. What is the partial pressure of the water vapor at the temperature of the experiment? What was the partial pressure of the hydrogen in the flask?

Calculate from these data:

1. The volume of the hydrogen under standard conditions of temperature and pressure.

2. The weight of the hydrogen. (The density of pure hydrogen under standard conditions is 0.0000899.)

3. The weight of zinc that would have liberated 1 gram atom of hydrogen. Compare this number with atomic weight of zinc.

From these conclusions write the equation for the reaction. The formula of sulfuric acid is $H_2SO_4$, and both hydrogens are replaced by zinc.

*Problems.* 1. (a) From the density of hydrogen calculate the weight of 22.4 liters of this gas under standard conditions. What is the true molecular weight of hydrogen? What is the formula of this gas? Have you written the above equation correctly?

(b) If you had not been given the density of hydrogen in the above experiment, how could you have calculated a value from the molecular weight? What percentage error would you have made?

2. (a) What weight of pure zinc sulfate ($ZnSO_4$) could be obtained from the weight of zinc used?

(b) What is the minimum weight of sulfuric acid ($H_2SO_4$) necessary in the experiment?

3. If hydrochloric acid (HCl) had been used instead of sulfuric acid, how much hydrogen would have been liberated? Write the equation. What weight of solid zinc chloride could have been obtained?

### *Note on Glass Manipulation.*

To bend a piece of ordinary glass tubing, hold it with both hands in a fan-shaped gas flame and rotate it slowly between the thumb and fingers until a 2½ to 3 inch portion is *uniformly* heated and is soft enough to be bent to the proper angle. Set it aside to cool; glass will remain hot enough to burn the hand for some time after it no longer appears to be hot.

To cut glass tubing, scratch it with a file at the proper place, grasp it firmly on each side of this mark (protecting the hands with a cloth), and bend the tube away from the mark.

Always remove the sharp edges of freshly cut glass at once with a file, or by heating in a gas flame.

To draw down a piece of tubing to a capillary, heat a portion about 1 inch long in an ordinary gas flame to a higher temperature than was necessary in bending the tubing. Hold the tube with both hands and rotate it to ensure uniform heating and prevent the hot portion from sagging. Withdraw from the flame and draw apart *slowly* to obtain a thick-walled capillary. Mount your piece of platinum wire (first used in Assignment VI) by inserting one end of the wire in the capillary near the tube, and heating until the glass closes firmly around the wire.

## ASSIGNMENT V.

### THE ANALYSIS OF COPPER OXIDE

(Two students work together.)

The purpose of Assignment V is to determine the relative weights of copper and oxygen in copper oxide. Hydrogen gas reacts with hot copper oxide to form metallic copper and steam. Two measurements are necessary: the weight of the copper oxide used, and the loss in weight when it is completely reduced to copper. *Question*: What does this loss of weight represent?

One of the students signs a white slip for "special apparatus for Assignment V", consisting of a thistle tube, a clamp, calcium chloride tube, with two rubber stoppers, 2 glass tubes, 2 rubber tubes, and 2 short glass rods, and returns the apparatus as soon as the experiment is finished.

Out of a wash bottle make a *hydrogen generator* by fitting it with a thistle tube (extending almost to the bottom of the flask) and an outlet tube bent at right angles (see note preceding this Assignment). Place in the wash bottle about 10 grams of zinc, and (to ensure a rapid reaction between Zn and $H_2SO_4$) cover with a very dilute solution of copper sulfate made by diluting 10 cc. of the laboratory solution to 100 cc. with water. To the outlet tube attach a "drying tube" (containing solid calcium chloride, which has the property of absorbing moisture). Make sure that the apparatus is airtight, and wrap the flask in a towel.

Set up the remainder of the apparatus according to the directions of the instructor. Dry the thick-walled glass tube that is to contain the copper oxide by heating it gently. When it is cool weigh it carefully, together with any portion of the apparatus that may come in contact with the copper oxide. Place in the tube about 1 gram of copper oxide, wipe off any particles that are not in the portion of the tube that is to be heated. Weigh again carefully to obtain the weight of copper oxide used. Attach the apparatus to the hydrogen generator, pour 10 cc. concentrated sulfuric acid (Caution!) down the thistle tube, and allow the hydrogen to pass through the apparatus until it has swept out the air. (*Caution!* Do not place a flame near the outlet nor heat the oxide while the apparatus contains a mixture of oxygen and hydrogen. A dangerous explosion might result.) Suggest a simple test to determine when the hydrogen is no longer mixed with oxygen.

When pure hydrogen is passing over the copper oxide, begin to heat it very gently with a small flame and continue to heat cautiously until all the oxide changes color. If moisture collects in the farther end of the tube drive it out by heating the tube carefully. *Question*: Where does this moisture come from?

Allow the tube to cool in the current of hydrogen, and weigh it. If you have time, check this result at once by repeating the heating and weighing; if not, set the tube aside in order that you may do so if the results of the following calculations are unsatisfactory.

From the results of your experiments calculate the percent of copper and oxygen in copper oxide.

How many grams of copper are combined with 1 gram atom of oxygen? Compare this figure with the atomic weight of copper. What, then, is the formula of this oxide of copper? Write the equation for the reaction. What is the true percent of copper and oxygen in this oxide of copper?

*Problems.* 1. (a) Another oxide of copper is known which contains 88.8% of copper. What is its formula?

(b) Which of the oxides is *cuprous* oxide and which *cupric oxide?*

(c) What are the formulas of cuprous and cupric sulfides?

(d) Two of the oxides of iron are FeO and $Fe_2O_3$: which is ferrous oxide and which is ferric oxide?

2 How many grams of water can be formed from 1 gram of cupric oxide? How many grams of hydrogen would be needed? What volume of hydrogen measured at 20° C and 1 atmosphere would be needed?

3. How many grams of zinc would be needed to generate enough hydrogen (by reacting with an acid) to reduce completely one gram molecule of cupric oxide? Compare this weight with the atomic weight of zinc.

## ASSIGNMENT VI.

### Properties of Aqueous Solutions of Acids and Bases.

(a) *Acids.* Prepare a solution of each of the common acids, hydrochloric, nitric and sulfuric, for use in the following experiments, by adding 50 cc. water to 5 cc. of the "dilute" laboratory solution of each of these acids. Label each solution.

*Taste.* Taste each solution by dipping a glass rod into the liquid and touching it to the tongue. (*Caution*: Do not taste any substance in the laboratory unless directed to do so.)

*Action on Indicators.* To about 20 cc. of distilled water in a beaker add enough blue *litmus* solution to give a distinct but not strong color. Divide this solution into three portions and to each add a few drops of a different acid.

Repeat, using *methyl orange* instead of litmus.

Withdraw a drop of any one of the acids on a glass rod and touch it to blue litmus paper.

Repeat, using red litmus paper.

*Action on Sodium Carbonate.* To 5 cc. of each acid in separate test tubes add a little powered sodium carbonate.

*Action on Metallic Zinc.* To 5 cc. of each acid add small pieces of zinc. Is the same gas given off in each case? Test it. Repeat the experiment with zinc and the ordinary laboratory solution of the acids.

Summarize the properties common to the acids you have studied. Note that any substance is recognized by its properties. Any solution which has the properties thus summarized is an acid solution and contains the substance hydrogen ion. The symbol is $H^+$.

In addition to the properties of hydrogen ion, the solution of each acid has another group of properties peculiar to itself by means of which the acids may be distinguished from one another. Try the following experiments:

To 15 cc. water add about 2 cc. silver nitrate solution. Divide the mixture into three portions and to each add a few cc. of a different acid.

In a similar set of experiments use barium chloride solution instead of silver nitrate.

State how the three acids may be distinguished.

Thus, in addition to hydrogen ion, hydrochloric acid solution contains *chloride ion,* $Cl^-$; nitric acid solution contains *nitrate ion,* $NO_3^-$; and sulfuric acid solution contains *sulfate ion,* $SO_4^{--}$.

Other properties of ions will be discussed in the lectures, and additional evidence of the existence of ions in aqueous solutions will be presented. The study of ionization will be continued in the laboratory in Assignment IX.

The chemical formulas of these three substances, whose aqueous solutions contain hydrogen ion, are:

| | |
|---|---|
| Hydrochloric acid | $HCl$, |
| Nitric acid, | $HNO_3$, |
| Sulfuric acid, | $H_2SO_4$. |

Calculate the molecular weight of each acid. Pure HCl is a gas, and it

is also named hydrogen chloride and hydrochloric acid gas. Pure $HNO_3$ and $H_2SO_4$ are liquids.

(b) *Bases.* To 5 cc. portions of the laboratory solutions of sodium hydroxide and potassium hydroxide (taken separately) add 50 cc. water. Use these two solutions and the undiluted laboratory solution of barium hydroxide in the following experiments:

*Taste.* Taste each of these three solutions by withdrawing a drop on a glass rod and touching it to the tongue.

*Touch.* Rub a drop of each solution between the thumb and finger.

*Action on Indicators.* Treat drops of each of the three solutions with red and with blue litmus paper.

To 5 cc. of each of the same solutions add a drop of litmus solution. To the sodium hydroxide solution containing the indicator add hydrochloric acid slowly and note the change of color. Then add sodium hydroxide solution until a change is noticed.

Repeat the last experiment, using fresh 5 cc. portions of the same hydroxide solutions and a solution of the indicator methyl orange.

Repeat, using a solution of the indicator phenolphthalein.

*Action with Ferric Chlcride Solution.* To 5 cc. portions of each of the hydroxide solutions add ferric chloride drop by drop.

Summarize the properties common to the solutions of the bases you have studied. Each solution contains the substance hydroxide ion, $OH^-$.

In addition to hydroxide ion the solution of each base also has properties characteristic of the base.

To 5 cc. of each hydroxide solution add a few drops of sulfuric acid.

Test a drop of each of the hyroxide solutions in a colorless gas flame by means of a looped platinum wire, as demonstrated by the instructor. Can the flame test be used to prove the presence of sodium?

State how these bases may be distinguished.

In addition to hydroxide ion, sodium hydroxide solution contains sodium ion, $Na^+$; potassium hydroxide contains potassium ion, $K^+$; and barium hydroxide contains barium ion, $Ba^{++}$.

Each of the hydroxides in the pure state is a solid. The chemical formulas for the hydroxides are:

Sodium hydroxide, $NaOH$,
Potassium hydroxide, $KOH$,
Barium hydroxide, $Ba(OH)_2$.

What is the molecular weight of each hydroxide?

Problems. 1. Make as simple a table as you can to show the colors obtained with different indicators in acid and basic solutions.

2. Four unlabelled beakers, which are known to contain solutions of sulfuric acid, nitric acid, barium hydroxide, and sodium hydroxide, are to be identified as quickly as possible. State what experiments you would perform, and note clearly the progress towards identification that would be made in each experiment.

## ASSIGNMENT VII.

### Reactions between Acids and Bases.

*Experiment.* Evaporate to dryness in a porcelain dish a few drops of (a) hydrochloric acid solution, (b) sodium hydroxide solution. In each case note if there is a residue, add a little water, and test the solution with an indicator. *Questions*: Taking into account that HCl and NaOH are both stable substances, state what gases were given off when the solutions were evaporated. What conclusion do you draw in regard to the *volatility* of hydrogen chloride and sodium hydroxide? How is sodium hydroxide pre-

pared from metallic sodium and water, hydrogen chloride from hydrogen and chlorine gases?

*Experiment.* To 10 cc. sodium hydroxide solution in a beaker add hydrochloric acid solution slowly until a drop of the mixture, after stirring, reacts acid to litmus paper. Evaporate in a porcelain casserole. While the solution is boiling, test again with litmus paper, and if the solution is no longer acid add HCl. When the solid begins to separate, use a small flame, and, if necessary, withdraw the flame and stir the mixture. Finally heat until the mixture is thoroughly dry. Allow the dish to cool, and note the appearance of the residue. Dissolve it in about 10 cc. of water. Test the solution with blue litmus paper and with phenolphthalein test a drop on a looped platinum wire in a colorless gas flame and test a small portion of the solution with silver nitrate in the presence of nitric acid. *Questions.* Does this solution have either acid or basic properties? What does the solution contain? What was the solid substance obtained on evaporation? What substances were volatilized? Why was hydrochloric acid added in excess instead of sodium hydroxide?

Write the equation (non-ionic) for the reaction between sodium hydroxide and hydrochloric acid, and state what has become of the hydrogen of the acid and the hydroxide radical of the base.

This reaction is typical of the action of any acid on any base.

Write the equations (non-ionic) for the following reactions, consulting a text-book if necessary.

1. Nitric acid and sodim hydroxide.
2. Sulfuric acid and sodium hydroxide.
3. Hydrochloric acid and barium hydroxide.

*Questions and Problems.* 1. Calculate the weight of sodium chloride that will be obtained on neutralizing one gram of sodium hydroxide with hydrochloric acid. How many molecules of HCl react with one molecule of $Ba(OH)_2$? What weight of barium hydroxide will be obtained on neutralizing one gram of barium hydroxide with hydrochloric acid?

2. What weight of barium hydroxide will react with one mol of hydrogen chloride? This is called one *equivalent* of barium hydroxide.

Suggest a similar definition for one *equivalent* of sulfuric acid from its reaction with sodium hydroxide. Note that one equivalent of any acid will react with one equivalent of any base and the resulting solution will contain one equivalent of a corresponding salt.

How many equivalents of barium hydroxide will react with one mol of sulfuric acid? How many equivalents of barium sulfate will be formed?

3. *Concentration of a Solution.* The concentration of a solution is the amount of the dissolved substance contained in a unit volume of the solution.

The molecular weight in grams (the *mol*) is frequently adopted as a unit of mass, and the liter is the standard unit of volume. A solution which contains in one liter one mol of the dissolved substance is called a *molal* solution.

How many grams of sulfuric acid are contained in a liter of a molal solution?

How many grams of sodium chloride are contained in a liter of a one-tenth molal solution? (0.1 *M* NaCl designates this solution.)

4. When we are dealing only with neutralization reactions it is convenient to use the equivalent (of the acid, or base, or salt) as the unit of mass. A solution which contains one equivalent in a liter is called a *normal* solution.

How many grams of HCl are contained in a liter of a 0.10 normal solution of hydrochloric acid (0.10 *N* HCl)?

How many grams of $Ba(OH)_2$ are contained in a liter of 0.10 *N* barium hydroxide solution?

How many cc. of 0.10 *N* HCl must be added to 100 cc. of 0.10 *N*

$Ba(OH)_2$ to produce a neutral solution of barium chloride? What color changes would be observed while the acid is being added to the barium hydroxide solution (1) if methyl orange were present, (2) if phenolphthalein were present?

## ASSIGNMENT VIII.

### Titration of Acids and Bases. An Illustration of Volumetric Analysis.

In Assignment VIII the purpose is to measure the volumes of solutions of acid and base which will exactly neutralize each other. This neutral point, called the end-point, is determined by means of some indicator like litmus or phenolphthalein. The whole experiment is called *titration*. *Question.*—Does the color of an indicator used in titration change gradually or suddenly as the solution is neutralized? If necessary, perform an experiment to determine this point.)

*Questions.* To what volume would you dilute 10 cc. of a 6-normal solution to prepare a 3-normal solution? How would you prepare a 0.5-normal solution from a 6-normal solution?

*Experiment.* Prepare about 400 cc. approximately 0.5-normal sodium hydroxide solution from the laboratory 6-normal solution. Place this 0.5-normal solution in your 500 cc. flask. Prepare also about 250 cc. approximately 0.5-normal sulfuric acid solution from the laboratory 6-normal solution, and place it in another flask. Cork and label each flask. Shake the flasks in order that the concentration of the solutions will be uniform throughout. Clean two other flasks, rinse them with distilled water, and set them aside to drain, in order that they may be ready for use later in the experiment; label one "known $H_2SO_4$ solution", and the other "unknown HCl solution".

*Note.* The volumes of the solutions used in a titration are measured by means of *burettes*. These are glass tubes, marked off in cubic centimeters and tenths (or fifths) of cubic centimeters, and provided with a glass tip out of which the solution may be drawn by opening a pinch-cock.

Apply at the office for two burettes and clamps, and return them the same day before the office closes. Sign a yellow temporary order slip when you receive these articles, and a blue return slip when you return them.

*Experiment.* Fill each burette with distilled water. Note that air may be removed from the small tube below the pinch-cock by tilting the tip upward and allowing the liquid to flow through the pinch-cock. Practice reading a burette: bring your eye to the same level as the liquid and note the reading of the burette corresponding to the bottom of the meniscus; repeat until consecutive readings check to better than 0.05 cc. *Question.* Why is it important to have the eye at the same level as the liquid before making a reading? Never attempt to adjust the volume of the solution in a burette so that the reading will be some exact amount. Allow the water to flow slowly out of the burette. If drops remain on the inner surface of a burette, exchange it at the office for a clean one.

Rinse one burette with a little of your approximately 0.5-normal $H_2SO_4$ solution, and fill the burette with this solution. Rinse and fill the other burette with the 0.5-normal NaOH solution.

Record the readings of the burettes side by side in your note-book; run about 10 cc. of the acid solution into a clean beaker or flask standing on white paper, and record the final burette reading under the initial reading. Add two drops of phenolphthalein, and about 20 cc. distilled water. Then run in the sodium hydroxide solution from the other burette, a little at a time, and towards the end, very carefully, a drop or two at a time, stirring the mixture constantly, until the faintest perceptible permanent pink color is

obtained. Wash down the inside of the beaker by means of a jet of water from the wash bottle. If too much of the basic solution is added, decolorize the solution by adding a little of the acid solution and determine the end-point again. Record the final readings of each burette, and the actual volumes of each solution used in the titration. Calculate the ratio of the two concentrations and state which is the more concentrated solution.

Repeat this experiment, using about 15 cc. and then about 20 cc. of the acid solution, and in each case make the same calculations. Do not fill up the burette before a titration unless there is not enough solution in it for the titration.

Compare the ratios of the concentrations calculated from these three titrations. If any result differs from the average by more than 1%, perform additional titrations until you are satisfied that you have determined the ratio of the concentrations with an accuracy better than 1%.

Take your two clean, dry, labelled flasks to the office to obtain a sulfuric acid solution of known concentration, and a hydrochloric acid solution whose concentration you are to determine.

Empty your acid burette, fill it with the sulfuric acid solution of known concentration, and determine as before from three (or more) titrations the relative concentrations of this solution and your sodium hydroxide solution. Never use less than 10 cc. of any solution in a titration. Calculate the concentration of your sodium hydroxide solution.

Finally titrate the unknown hydrochloric solution against the same sodium hydroxide solution, and calculate the concentration of the acetic acid solution. Report this result at once to your instructor. If the result is not sufficiently accurate, first look for an error in your calculations, but, if necessary, repeat the experiment.

Make a list of the sources of error. (Many of them have been mentioned in the above directions.)

Save the remainder of the NaOH solution,whose concentration you have determined, in a corked flask for use in Assignment X.

*Problems.* 1. If the error in measuring out a volume of solution by means of a burette is 0.10 cc. what is the percentage error if 1 cc. of solution is measured? If 20 cc. of solution are measured? Why is it important not to use less than 10 cc. in any titration?

2. How many cubic centimeters of 1 *molal* sulfuric acid will contain 0.01 equivalent? How many *grams* of sodium hydroxide would be needed to neutralize this amount of acid?

3. Chemically pure ("C. P.") sulfuric acid, nitric acid, hydrochloric acid and ammonia, as supplied by the manufacturers, are concentrated aqueous solutions of these substances. The concentration of each solution is guaranteed not to be less than a certain minimum value, and this is tested by measuring the density (specific gravity). The following table contains the density and the percentage composition by weight of the concentrated laboratory reagents.

| | Density | % by weight | Normal Concentration |
|---|---|---|---|
| $H_2SO_4$ | 1.84 | 95.6% $H_2SO_4$ | |
| $HNO_3$ | 1.42 | 69.8% $HNO_3$ | |
| HCl | 1.19 | 37.2% HCl | |
| $NH_4OH$ | 0.90 | 28.3% $NH_3$ | |

For each reagent calculate the normal concentration and record the results in the fourth column of the table.

*CAUTION!* The concentrated acids, especially sulfuric and nitric, produce dangerous burns and should not be used carelessly. These reagents are kept on lead shelves and must not be used unless special directions are given.

## ASSIGNMENT IX.

### Strong Acids. Ionic Equations.

In Assignments VI and VII the general properties of acids and bases were studied, and it was recognized that acid solutions contain hydrogen ion, and basic solutions hydroxide ion. The purpose of Assignments IX and X is to compare the concentrations of hydrogen ion in solutions of different acids and to introduce the writing of ionic equations.

*Experiment.* Prepare a one-normal solution (about 60 cc.) hydrochloric acid from the 6 *N* laboratory reagent (see questions below) and from this solution prepare about 50 cc. each of 0.10 *N*, .01 *N* and .001 *N* solutions. Be careful to shake each solution after preparing it from a more concentrated solution and water.

*Questions.* What volume of 6 *N* acid is needed to make 100 cc. of 1 *N* acid?

How much water should be added to 10 cc. of 6 *N* acid to make 1 *N* acid?

How much water should be added to 10 cc. of 1 *N* acid to make 0.10 *N* acid?

What volume of 0.01 *N* acid can be made from 5 cc of 0.1 acid?

If hydrochloric acid is ionized completely what is the concentration of hydrogen ion and of chloride ion in each of the solutions prepared?

*Experiment.* Pour into marked test tubes 10 cc. of each solution (*N*, 0.1 *N*, 0.01 *N* 0.001 *N*), and pour 10 cc. of water into a fifth test tube. Add to each solution from a glass tube a single drop of *methyl violet* solution. Hold the tubes in a vertical position, look down at the surface of the solutions, record the color of each solution, and note the smallest concentration of hydrochloric acid that shows with this indicator a different color from water.

State how the indicator, methyl violet, may be used to determine the approximate concentration of a hydrochloric acid solution. (The color in the more concentrated solutions will fade on standing. It may be restored by adding another drop of the indicator.) Set the 0.01 *N* solution aside for use in a later experiment (Assignment XIII).

Repeat the experiment with nitric acid and with sulfuric acid, starting in each case with the 6 *N* laboratory acid. Compare the colors obtained with the different acids. *Questions.* Are the colors characteristic for each acid? If not, what substance determines the color? If hydrochloric acid is completely ionized what conclusion can you draw with respect to the ionization of nitric acid and sulfuric acid? Do these experiments prove that these three acids are highly ionized?

Summarize briefly the evidence presented in the lectures that these acids, the bases sodium hydroxide and potassium hydroxide, and nearly all salts are highly ionized in dilute solutions. Such substances are called *strong electrolytes,* these three acids are *strong acids,* and sodium hydroxide is a *strong base.* The term strong salt is seldom used, because there are so few slightly ionized salts. In pure water the concentration of $H^+$ and $OH^-$ ions is extremely small and it is an example of a very *weak electrolyte.*

We shall next consider what ionic reaction takes place when a strong acid neutralizes a strong base. The equation,

$$H_2SO_4 + 2NaOH = 2H_2O + Na_2SO_4,$$

which we have been using hitherto, states that 1 mol or 2 equivalents of sulfuric acid and 2 mols or 2 equivalents of sodium hydroxide react, and that the resulting solution contains 1 mol or 2 equivalents of the salt sodium sulfate, and 2 more mols of water than were formerly present; but it does not show the difference between the ions present in the two initial solutions and in the final solution. This difference may be stated in words, or expressed briefly in the following equation:

$$(2H^+ + SO_4^{--}) + (2Na^+ + 2OH^-) = 2H_2O + 2Na^+ + SO_4^{--}.$$

The $Na^+$ and $SO_4^{--}$ are the same in the initial and final solutions, and it is not correct to say that they have *united* to form $Na_2SO_4$. The reaction that has taken place is

$$H^+ + OH^- = H_2O.$$

This equation states that 1 mol or 1 equivalent of hydrogen ion has combined with 1 mol or 1 equivalent of hydroxide ion to form 1 mol of water. Write the ionic equations for the neutralization of hydrochloric acid and nitric acid solutions by sodium hydroxide solution. State briefly the evidence presented in the lectures to show that the reaction between any strong acid and any strong base is the same in all cases. What reaction will take place whenever a solution with acid properties is mixed with a solution that has basic properties?

*Problems.*—1. Write ionic equations for the following reactions:

(a) A sodium chloride solution is evaporated to dryness (solids are not ionized).

(b) A sodium sulphate solution is evaporated to dryness.

(c) Hydrogen chloride gas is dissolved in water (gases are not ionized).

(d) A precipitate of silver chloride, AgCl, is formed by mixing solutions of silver nitrate and sodium chloride.

(e) A precipitate of barium sulfate, $BaSO_4$, is formed by mixing solutions of barium chloride and sodium sulfate.

2. Does anything happen in the following experiments?

(a) Dilute solutions of sodium chloride and potassium nitrate are mixed.

(b) Dilute solutions of sodium chloride and nitric acid are mixed.

3. What is the concentration of $Na^+$, of $Cl^-$, in a solution prepared by dissolving 1.17 grams sodium chloride in 1 liter of water?

## ASSIGNMENT X.

### Weak Acids. Equilibrium.

*Experiment.* Prepare normal and 0.1 normal acetic acid solutions* from the laboratory 6-normal solution.

Determine if the 0.1 normal acetic acid soution has acid properties by testing it with litmus, methyl orange, sodium carbonate, and by tasting it (Cf. Assignment VI).

Estimate approximately the concentration of hydrogen ion in the normal and 0.1 normal acetic acid solutions by testing 10 cc. of each solution with a a drop of methyl violet solution, and comparing the colors with those obtained with hydrochloric acid solution and water in the preceding Assignment. *Notes and Questions.* The reasoning depends upon the comparison of the lowest concentration of solutions of the two acids at which methyl violet gives a color distinctly different from that with water. The acetic acid in the solution must be present either in the form of ions, $H^+$ and $Ac^-$, or in the un-ionized form, HAc. From your estimate of the concentration of $H^+$ in the 0.1 normal solution, calculate the fraction which is ionized, and the fraction which is un-ionized. The fraction of the acid which is in the form of ions is called the *degree of ionization.* State also the concentrations of acetate ion, $Ac^-$, and of the un-ionized acid, HAc, in the 0.1 normal acetic acid solution. Is acetic acid a weak or a strong acid?

*Questions.* The concentration of the ions in acetic acid solutions have been determined more accurately than is possible by these color experiments.

* Save some 0.1 normal acetic acid solution for use in Assignment XIII.

The concentrations of hydrogen ion in these solutions at room temperature are given in the following table.

| Concentration of acid. | Concentration of $H^+$. | Concentration of $Ac^-$. | Concentration of un-ionized HAc. | Degree of Ionization. |
|---|---|---|---|---|
| 1 $N$ | .004 $N$ | | | |
| 0.5 $N$ | .003 $N$ | | | |
| 0.1 $N$ | .0013 $N$ | | | |

Fill in the remaining columns of the table. Does the degree of ionization decrease or increase as the concentration of the acid decreases?

In any given solution containing acetic acid each of the substances, $H^+$, $Ac^-$, and HAc, has a definite concentration. The three substances are in equilibrium, and their concentration may be changed by altering the experimental conditions, e. g., by raising or lowering the temperature, or by increasing or decreasing the concentration of one or more of the substances involved. A careful study of this equilibrium will enable the student to understand more readily the many other examples of equilibrium that will be met with in this course.

First consider the restriction that these three substances are not independent of each other,—since, namely, $H^+$ and $Ac^-$ form HAc when they unite, and HAc forms $H^+ + Ac^-$ when it ionizes. It is important to realize that whenever there is a disturbance of this equilibrium, either the ions unite to form un-ionized HAc, or HAc breaks up into the ions. These ideas are all involved in the statement that

$$H^+ + Ac^- = HAc$$

is a *reversible reaction;* and the problem is to determine how the reaction may be made to proceed to the right or to the left.

*Questions.* What reaction takes place (a) when acetic acid gas is dissolved in water, (b) when water is added to a normal solution of acetic acid? In the latter case consider the degrees of ionization which you calculated for acetic acid at different concentrations.

*Experiment.* The reaction between sodium acetate and hydrochloric acid. —Prepare some approximately half normal hydrochloric acid. Measure out three 15 cc. portions in test tubes, and add two or three drops of methyl violet to each. Measure out 5 cc. 2 $N$ sodium acetate solution and add the solution, a few drops at a time, to one of the 0.5 $N$ hydrochloric acid solutions; shake the mixture after each addition, recording the color and estimating the volume of the sodium acetate solution added. Repeat the experiment to check your results. What conclusions can you draw with regard to changes in the hydrogen ion concentration? (Note that sodium acetate, like other salts, is present in solution as ions, in this case $Na^+$ and $Ac^-$.) State what reaction has taken place and write the equation. Could the result of this experiment have been predicted from your previous experiments on acetic acid in this Assignment?

*Experiment.* The reaction between sodium acetate and acetic acid.—Predict what will happen when sodium acetate solution is added to acetic acid solution. Give your reasoning. Test your answer experimentally by adding 2 $N$ sodium acetate solution to normal acetic acid containing a drop of methyl violet.

Review the lectures on equilibrium while answering the following problems.

*Problems.* 1. A vessel is partially filled with water; all the air in it is removed, and the vessel is closed. What is the total pressure in the vessel at 22° (see Vapor Pressure of Water, Table, Assignment III)? What will the total pressure become if the vessel is heated to 30°? How has the weight of water

vapor in the vessel changed (qualitatively)? What reaction has taken place during the change from 22° to 30°? If the vessel is again brought to 22° what will be the pressure? Write the reaction that has taken place during cooling. Suggest a method for making this reaction go in either direction without changing the temperature.

2. State in words what is represented by each of the following equations. Suggest experimental conditions under which each reaction can be made to proceed (1) towards the right and (2) towards the left. Under what conditions will equilibrium be established in each case?

(a) $HCl$ (gas) $= H^+ + Cl^-$ (in solution)

(b) $Zn$ (solid) $+ H_2O$ (gas) $= ZnO$ (solid) $+ H_2$

3. Are the gases, hydrogen, oxygen, and nitrogen slightly soluble or very soluble in water? Give reasons for your answers. What happens when water saturated with one of these solutions is boiled? How is the equilibrium between the gas phase and the solution altered by an increase of temperature? What substances are present in solutions of each of these gases?

## ASSIGNMENT XI.

### Neutralization of Acetic Acid Solution by a Strong Base.

The purpose of Assignment XI is to study the reaction between solutions of acetic acid and of the strong base, sodium hydroxide, and continue the writing of ionic equations.

*Question.* How many grams of acetic acid are contained in a liter of molal solution? The formula is $HC_2H_3O_2$.

*Experiment.* Procure two burettes at the office, fill one with your sodium hydroxide solution of known concentration (Assignment VIII), and the other with the special acetic acid solution marked for use in this Assignment. The concentration of the latter solution is in the neighborhood of molal; the exact value will be announced. Titrate the two solutions, using phenolphthalein as indicator, and save the solutions obtained in the titrations. Note if the end-point is sharp, and if the results of two or more titrations are concordant. Calculate the normal concentration of the acetic acid solution. *Questions.* What conclusions do you draw from your results? How many mols of acetic acid are neutralized by 1 equivalent of sodium hydroxide?

*Experiment.* Acidify the solution obtained in one of the above titrations with a little acetic acid, and evaporate it to dryness, taking care not to heat the residue strongly while driving off the last portions of water and acetic acid. *Questions.* What is the solid residue? From the results of the titrations write the equation (non-ionic) for the neutralization of acetic acid by sodium hydroxide. Point out how it is possible for this solution of a weak acid, in which the concentration of $H^+$ is so small, to neutralize so much sodium hydroxide. Which is the weaker electrolyte, acetic acid or water?

If you have answered the questions in the preceding paragraph correctly you will realize that it is impossible to represent all that has happened in this neutralization reaction in a single equation. However, by following the plan adopted in Assignment IX we can find the one equation that shows most satisfactorily the difference between the initial solutions and the final solution.

$$HC_2H_3O_2 + (Na^+ + OH^-) = H_2O + Na^+ + C_2H_3O_2^-.$$

This equation shows that $NaOH$ and $NaC_2H_3O_2$ are strong electrolytes, that the weak acid is mainly present in the un-ionized form, and that the sodium ion takes no part in the reaction. Accordingly the equation

$$HC_2H_3O_2 + OH^- = H_2O + C_2H_3O_2^-$$

represents the main reaction. It tells nothing, however, about the "mechanism" of the reaction.

*Problems.* 1. How many grams of sodium acetate can be prepared (a) from 50 cc. normal acetic acid solution, (b) from 100 cc. 0.5 normal acetic acid solution?

2. Outline experiments to distinguish between

(a) 1.0 $N$ $HNO_3$ and 0.1 $N$ $HNO_3$,
(b) 0.01 $N$ $HNO_3$ and 1.0 $N$ acetic acid.

*Optional Experiment.* This is to be ommitted by the majority of the class, and should not be porformed without consulting the instructor. Repeat the titration of the acetic acid and sodium hydroxide solutions, using methyl orange as indicator.

## ASSIGNMENT XII.

### Strong and Weak Bases. Equilibrium.

The purpose of Assignment XII is to compare the concentration of hydroxide ion in solutions of different bases, and to continue the study of equilibrium.

*Experiment.* Prepare solutions of sodium hydroxide which are approximately normal, 0.1 normal, 0.01 normal, and 0.001 normal. (State in your note-book how you prepared these solutions.) To 10 cc. of each solution in a test tube, add 1 drop of a solution of the indicator, *trinitrobenzol.* Record the color obtained in each case, and note carefully the most dilute solution that gives a color with the indicator.

Repeat the experiment with potassium hydroxide solution, and compare the colors obtained at each concentration. If sodium hydroxide in solution is completely ionized, what conclusion can you draw with respect to potassium hydroxide? What concentrations of *hydroxide ion* can be measured by means of this indicator, trinitrobenzol?

Try similar experiments with ammonium hydroxide solutions of various concentrations, say normal and 0.1 normal*. Point out the sodium hydroxide solution and the ammonium hydroxide solution which give approximately the same *faint* color with the indicator, and estimate the concentration of hydroxide ion in this ammonium hydroxide solution. What is the concentration of ammonium ion $NH_4^+$ in this solution? What is the concentration of the un-ionized ammonium hydroxide, $NH_4OH$? What is the "degree of ionization"? Is ammonium hydroxide a strong or a weak base?

In every solution of ammonium hydroxide, just as in the case of acetic acid, there is a definite equilibrium between the un-ionized substance and the two ions. This equilibrium is represented by the equation

$$NH_4OH = NH_4^+ + OH^-.$$

Taking into account the results obtained in these experiments, predict what will happen when solutions of sodium hydroxide and ammonium chloride are mixed. Test your answer by means of an experiment with these solutions and the indicator, trinitrobenzol. Write an equation for the reaction that takes place.

How will the equilibrium in an ammonium hydroxide solution be disturbed when ammonium chloride is added? What reaction will take place? Test your answer by an experiment with 1 normal $NH_4OH$, ammonium chloride solution and trinitrobenzol.

*Problems.* 1. An ammonium hydroxide solution has a characteristic odor; this is due to the $NH_3$ gas given off by the solution. Which solutions

*Save some 0.01 normal NaOH and 0.1 normal $NH_4OH$ solutions for use in Assignment XIII.

smell more strongly of ammonia, (a) a dilute solution or a concentrated solution? (b) a cold solution or a hot solution? Write an equation to show the formation of $NH_4OH$ from $NH_3$ and water. Is this a reversible reaction? Is there an equilibrium between gaseous $NH_3$ and the solution? Give reasons for your answers. In this discussion point out what happens (a) when $NH_3$ gas is passed into pure water, (b) when the resulting solution is boiled in an open vessel, (c) when the gas space above a solution is evacuated.

2. How will the equilibrium $NH_4OH = NH_4^+ + OH^-$ be disturbed when sulfuric acid is added to an ammonium hydroxide solution? State how you would prepare ammonium sulfate from ammonium hydroxide and sulfuric acid. Write an equation to represent the main reaction in aqueous solution.

## ASSIGNMENT XIII.

### Hydrolysis.

In earlier Assignments neutralization reactions have been shown to depend upon the fact that the reaction $H^+ + OH^- = H_2O$ takes place practically completely. The concentration of $H^+$ and $OH^-$ in pure water is, however, not zero; each has a definite, although very small, value, namely $10^{-7}$ $N$ ($1/10^7$). Water is accordingly a very weak electrolyte; in other words, the reaction between $H^+$ and $OH^-$ does not go quite to completion, and there is in all aqueous solutions an equilibrium

$$H_2O = H^+ + OH^-.$$

In Assignment XIII we shall study some experiments closely connected with this fact.

A solution of sodium acetate may be prepared in two ways: (1) by mixing *exactly equivalent* amounts of acetic acid and sodium hydroxide (reaction, $HAc + Na^+ + OH^- = Na^+ + Ac^- + H_2O$, or more simply, $HAc + OH^- = Ac^- + H_2O$), and (2) by dissolving solid sodium acetate in water. Both solutions must have exactly the same properties.

Prepare some 0.01 $N$ NaOH, 0.01 $N$ HCl, 0.1 $N$ acetic acid, and 0.1 $N$ ammonium hydroxide for use in the following experiments.

*Experiment.* To 10 cc. 4 $N$ sodium acetate solution add one drop litmus solution. To another 10 cc. portion of the solution add one drop phenolphthalein solution. Repeat with 10 cc. portions of distilled water. What results did you obtain in similar experiments with NaCl solution in Assignment VII? (Repeat these experiments if necessary.)

*Questions.* In what respect does the sodium acetate solution differ in properties from water and from a sodium chloride solution? Is the reaction between equivalent amounts of acetic acid and sodium hydroxide complete? What substances are present in the resulting solution? State what happens when solid sodium acetate is dissolved in water. The reaction that takes place between the acetate ion and water is an example of *hydrolysis.* Write this reaction as well as you can in a single equation, and compare the equation with that given above for the neutralization of acetic acid by sodium hydroxide. Which of the following substances in the 4 $N$ sodium acetate solution have (1) large concentrations, (2) small concentrations, and (3) extremely small concentrations: $H_2O$, $Na^+$, $Ac^-$, HAc, $OH^-$, $H^+$. Test your answer by the following experiments:

*Experiment.* To 10 cc. 4 $N$ sodium acetate solution containing 1 drop phenolphthalein add 0.1 $N$ acetic acid, drop by drop. State in words what happens in this reaction. Write the equation for the main reaction.

*Experiment.* To 10 cc. distilled water containing 1 drop phenolphthalein add 0.01 $N$ NaOH solution drop by drop until (after shaking) the color is the

same as in the 4 $N$ NaAc solution. Estimate the volume of one drop by counting the number of drops in, say 5cc., and calculate the concentration of hydroxide ion in 4 $N$ sodium acetate. What is the concentration of un-ionized acetic acid in the same solution? What is the concentration of $Na^+$ and of $Ac^-$? (Assume complete ionization of sodium acetate and sodium hydroxide.)

*Questions.* Do these results furnish any evidence that the reaction $H^+ + OH^- = H_2O$ is reversible? How is this equilibrium disturbed by the addition of sodium hydroxide? Is the concentration of hydrogen ion in the 4 $N$ sodium acetate solution greater or less than in pure water?

*Experiment.* Repeat the above experiments with 10 cc. 4 $N$ ammonium chloride. State whether the solution has an acid or basic reaction.

To 10 cc. of 4 $N$ ammonium chloride containing a drop of litmus solution add gradually 0.1 $N$ $NH_4OH$ until the solution is neutral. What reaction has taken place? Discuss the hydrolysis of ammonium chloride and the neutralization of the weak base ammonium hydroxide by an equivalent amount of hydrochloric acid. Write a single equation to represent the main reaction in each case. Devise and try an experiment to determine the hydrogen ion concentration in 2 $N$ ammonium chloride.

*Questions.* How do the concentrations of $H^+$ and $OH^-$ in pure water and in solutions of NaCl, $NaNO_3$, $K_2SO_4$, compare with each other? What conclusions can you draw with regard to (a) the hydrolysis of the salt of a strong acid and a strong base, (b) the hydrolysis of the salt of a weak acid and a strong base, as potassium acetate, (c) the hydrolysis of the salt of a strong acid and a weak base, as ammonium nitrate?

State whether or not you would expect a salt of a weak acid and a weak base (as ammonium nitrate) to be hydrolyzed. Ammonium acetate, like other salts, is completely ionized in dilute solution. When solid ammonium acetate is dissolved, what reaction will take place between (1) ammonium ion and water, (2) between acetate ion and water? Write a single equation to represent the hydrolysis. Will the neutralization reaction between equivalent amounts of acetic acid and ammonium hydroxide take place completely? Will it take place more or less completely than the neutralization of acetic acid by sodium hydroxide?

*Experiment.* Test a normal solution of ammonium acetate with indicators. Explain your results, taking into account the fact that acetic acid and ammonium hydroxide are ionized to about the same extent.

*Problems.* 1. In the table given below fill in the formulas of the compounds which the given positive and negative ions form with each other.

Now mark with a star (*) those compounds which are only slightly ionized in solution, and mark with an "h" those compounds which are hydrolyzed in solution.

Study this table carefully and point out parallelisms between the strengths of acids and bases and the hydrolysis of the corresponding ions.

| | $H^+$ | $Na^+$ | $K^+$ | $NH_4^+$ |
|---|---|---|---|---|
| $OH^-$ | | | | |
| $Cl^-$ | | | | |
| $NO_3^-$ | | | | |
| $SO_4^{--}$ | | | | |
| $Ac^-$ | | | | |

2. Summarize the behavior of solutions towards the five indicators you have used in Assignments VI to XIII by completing the following table.

| Concentration. | Methyl violet. | Methyl orange. |
|---|---|---|
| $H^+$ 1.0 normal | yellow | red |
| $H^+$ 0.1 " | | " |
| $H^+$ 0.01 " | | " |
| $H^+$ 0.001 " | violet | " |
| $H^+$ slightly greater than in water | " | red |
| $H^+$ and $OH^-$ equal in water | " | yellow |
| $OH^-$ slightly greater than in water | | " |
| $OH^-$ 0.01 normal | | " |
| $OH^-$ 0.1 " | | |
| $OH^-$ 1.0 " | | |

State how you would estimate roughly the $H^+$ or $OH^-$ concentration in any colorless unknown solution. Suggest a definition for an indicator.

## ASSIGNMENT XIV.

### Carbon Dioxide, Carbonates, Bicarbonates, Carbonic Acid.

In Assignments VI and X solutions of acids were found to react with sodium carbonate to give a colorless, odorless gas. This gas is carbon dioxide, $CO_2$. In Assignment XIV we shall study this reaction more carefully, and shall investigate the behavior of an aqueous solution of carbon dioxide.

*Experiment.* Add a small quantity of powdered sodium carbonate, $Na_2CO_3$, to 10 cc. water, shake the mixture several times, and filter if there is a residue. Add some of the clear solution, a little at a time, to a solution of (a) hydrochloric acid, (b) acetic acid. Is $Na_2CO_3$ a readily soluble or a difficultly soluble substance? Like other salts, it is highly ionized in aqueous solution. Complete the equations

$$H^+ + CO_3^{--} = CO_2 +$$
$$HAc + CO_3^{--} = CO_2 +$$

*A Test for Carbon Dioxide.* Moisten the end of a glass tube with $Ba(OH)_2$ solution and hold it over a solution from which $CO_2$ bubbles are issuing (or pass $CO_2$ gas into 1 or 2 cc. $Ba(OH)_2$ solution). The white solid is barium carbonate, $BaCO_3$, and its formation from $Ba(OH)_2$ solution is a test for carbon dioxide. Prove that the breath contains $CO_2$. Is $BaCO_3$ readily soluble or difficultly soluble in water? Complete the equation

$$CO_2 + Ba^{++} + OH^- = BaCO_3 +$$

Note that $Ba(OH)_2$ is a strong base. Outline an experiment to prove this.

*Experiment.* Repeat the first experiment, using sodium bicarbonate, $NaHCO_3$, instead of $Na_2CO_3$. Report whether it is readily soluble or difficultly soluble in water. Prove that the gas evolved is $CO_2$. Complete the equations

$$H^+ + HCO_3^- = CO_2 +$$
$$HAc + HCO_3^- = CO_2 +$$

and compare them with the equations for the corresponding reactions with carbonate ion.

*Experiment.* Limestone is calcium carbonate, $CaCO_3$. Is it readily or difficultly soluble in water? Try an experiment, if necessary. Test the action of hydrochloric and acetic acid on small amounts of solid calcium carbonate, and complete the equations

$$H^+ + CaCO_3 \text{ (solid)} =$$
$$HAc + CaCO_3 \text{ (solid)} =$$

State what you think will happen when solid $BaCO_3$ is treated with hydrochloric acid. Try the experiment and write the equation for the reaction.

Set up a *carbon dioxide generator* similar to that used in preparing hydrogen (Assignment V); sign a white slip for the thistle tube. Place in the flask a few small lumps (about 5 grams) of limestone, cover with water, and add a little hydrochloric acid through the thistle tube.

Show by experiments:

Whether $CO_2$ is denser or lighter than air.

Whether it is inflammable or supports combustion.

Whether or not it dissolves in water. Give details of the last experiment.

The solution of carbon dioxide in water contains *carbonic acid,* $H_2CO_3$. Prove by experiment that

$$CO_2 \text{ (gas)} + H_2O = H_2CO_3 \text{ (in solution)}$$

is a reversible reaction, and that therefore is an equilibrium. At room temperature a solution in equilibrium with $CO_2$ gas at 1 atmosphere pressure contains about 0.04 mol $H_2CO_3$ in 1 liter. How is this equilibrium altered by an increase of temperature?

*Properties of a Solution of Carbonic Acid.* Prepare a small quantity of a nearly saturated solution of $CO_2$ and test it with indicators (see Problem 2, Assignment XIII). Is $H_2CO_3$ a weak or a strong acid? Decide if possible whether it is weaker or stronger than acetic acid. The equilibrium in the solution depends on the reversible reaction

$$H_2CO_3 = H^+ + HCO_3^-.$$

Explain what happens in the following experiments:

To 10 cc. water add 1 drop litmus solution,—just enough to give a faint bluish color. Pass in $CO_2$ gas until the color changes. Heat the solution to boiling and cool it again.

To 10 cc. water containing 1 drop phenolphthalein add a drop of dilute NaOH solution,—just enough to give a faint pink color; pass in $CO_2$ gas.

Review the above experiments on the action of acids on $NaHCO_3$ solution, $Na_2CO_3$ solution, and solid $CaCO_3$, and state what happened in the solution before $CO_2$ gas was evolved.

*The Neutralization of Carbonic Acid in Steps.* Which of the following equations represents the main reaction when solutions of equimolal quantities of $H_2CO_3$ and NaOH are mixed?

$$H_2CO_3 + OH^- = HCO_3^- + H_2O$$
$$H^+ + OH^- = H_2O$$

*Experiment. The reaction between bicarbonate ion and hydroxide ion.*—To a solution of sodium bicarbonate containing trinitrobenzol, add slowly from a graduated cylinder 0.5 normal NaOH solution. Perform a blank experiment (for comparison) by adding the NaOH solution to an equal volume of water containing the same indicator. Have you any evidence that the reaction

$$HCO_3^- + OH^- = H_2O + CO_3^{--}$$

has taken place? Is it correct to say that bicarbonate ion is an acid? Try to devise an experiment to test if the reaction just written is reversible.

Write the equation for the main reaction between $H_2CO_3$ and excess sodium hydroxide solution.

*Experiment. The hydrolysis of carbonate ion.*—Test 10 cc. portions of normal $Na_2CO_3$ solution with indicators. To the portion containing phenolphthalein add 0.1 normal hydrochloric acid very slowly from a graduate. Compare your results with those obtained with sodium acetate solutions in Assignment XIII, and state which solution has the greater concentration of $OH^-$. The reaction between carbonate ion and water is

$$CO_3^{--} + H_2O = HCO_3^- + OH^-,$$

and this experiment furnishes a proof that $HCO_3^-$ is a very weak acid. Which is the weaker acid, acetic acid or bicarbonate ion? Give your reasoning.

It is evident from the preceding experiments that the weak dibasic acid $H_2CO_3$ ionizes in two stages, namely,

$$H_2CO_3 = H^+ + HCO_3^-, \text{ and}$$
$$HCO_3^- = H^+ + CO_3^{--}.$$

The second acid, $HCO_3^-$, is a much weaker acid than the first, $H_2CO_3$. Suggest experiments or give reasons to prove this fact. There are two series of salts: the "normal salts" as $Na_2CO_3$ and $CaCO_3$ and the "acid salts" as $NaHCO_3$. The chief negative ions present in solutions of these two types of salts are $CO_3^{--}$ and $HCO_3^-$ respectively. Sodium bicarbonate is also named sodium acid carbonate or sodium hydrogen carbonate; and the bicarbonate ion is named similarly the acid carbonate ion or the hydrogen carbonate ion.

The behavior of other *weak polybasic acids* is similar to that of carbonic acid. Thus the weak dibasic acid, hydrogen sulfide in solution, $H_2S$, ionizes in two stages, and there are two series of salts. The second acid, $HS^-$, is weaker than the first, $H_2S$.

Sulfuric acid, $H_2SO_4$, is an example of a strong polybasic acid. Review your experiments with $H_2SO_4$ in Assignments VIII, and IX, and decide whether hydrogen sulfate ion, $HSO_4^-$, is a strong or a weak acid. What ions are present in large quantity in a dilute solution of potassium acid sulfate, $KHSO_4$? Try experiments if necessary.

*Problems.* 1 What general statement can you make about the action of an acid on a solution of a salt of a weaker acid? Give examples and write equations.

2. A solution of sodium bicarbonate is prepared by dissolving 8.4 grams of this salt in enough water to give 1 liter of solution. (a) Calculate approximately the concentration of $HCO_3^-$ in this solution. (b) What weight of sodium carbonate can be prepared from this solution? (c) How many cc. of normal NaOH solution are necessary in (b)? What volume of $CO_2$ under standard conditions can be prepared from this quantity of $NaHCO_3$?

*Optional Experiment.* Test a solution of $NaHCO_3$ with indicators.

Considering the facts that $H_2CO_3$ is a stronger acid than $HCO_3^-$, predict what will happen when $CO_2$ is passed into a solution of $Na_2CO_3$. Test your answer experimentally. Write the equation for the reaction.

Predict what will happen when a solutoin of $NaHCO_3$ is boiled. How would the concentration of $OH^-$ change during the boiling? Test your answer by experiments. Write the equation or equations. Is the reaction considered in the preceding paragraph reversible?

*Note.* When you have completed Assignment XIV, clean your two sample bottles, label them with your desk number and name, mark them No. 1 and No. 2 respectively, and deposit them at the office. Your two unknowns (for analysis) will be ready for you at the next laboratory period. See Assignment XV.

## ASSIGNMENT XV.

### Review. Analysis of Solutions for Ions Already Studied.

Give formulas and names of four or five of the common sodium, potassium and ammonium salts. Are these salts readily soluble or difficultly soluble in water? Are all of them highly ionized in dilute solution?

What is the color of each of the ions, $Na^+$, $K^+$, $NH_4^+$? Give other properties of these ions, and specify a characteristic property of each that may be used as a test. Devise methods of testing for each of these ions in the presence of the other two. Try your methods with known solutions: for example, divide a solution contining $Na^+$ and $NH_4^+$ into two parts, to one part add a

small quantity of a potassium salt solution, and be sure that you can distinguish between these two solutions. Is it $Na^+$ or $NH_4^+$ that causes difficulty in testing for $K^+$?

Suggest a method of testing a solution for the presence of a carbonate based on the evolution and detection of $CO_2$. Try your method.

State how you would test a solution for the presence of $Cl^-$, for the presence of $SO_4^{--}$. Write the ionic equations. Apply these tests to a solution of a carbonate free from $Cl^-$ or $SO_4^-$ in order to determine if carbonate interferes with your tests. If it does, suggest and try a method of preventing this interference.

*Experiment.* Heat to boiling a normal solution of $(NH_4)_2SO_4$ in a small beaker, and note if there is an odor. Now add 1 cc. 6 normal NaOH, and again heat to boiling. While you are heating the mixture note the odor and test the vapor with moist litmus. *Questions.* What reaction takes place (a) when cold solutions of $(NH_4)_2SO_4$ and NaOH are mixed? (b) when the solution is boiled? What volume of 6 normal NaOH would be needed to react completely with 5 cc. normal $(NH_4)_2SO_4$? If a mixture consisting of 5 cc. normal $(NH_4)_2SO_4$ and 3 cc. 6 normal NaOH were evaporated to dryness, what substances would be present in the solid residue?

*Experiment.* Mix 5 cc. normal NaCl and 3 cc. 6 normal $H_2SO_4$ in your casserole, evaporate the mixture on the porch* until heavy white fumes of sulfuric acid are given off. When the residue is cold, pour it into cold water, and test the solution for chloride. *Questions.* Did any reaction take place (a) when the two solutions were mixed, (b) when the mixture was evaporated? Which is the more volatile, HCl or $H_2SO_4$?

Test the volatility of nitric acid and acetic acid by evaporating solutions of these acids in a porcelain dish on the porch.

Salts of sodium and potassium, and of metals in general, are not easily volatilized. Test the volatility of ammonium salts, as $NH_4Cl$ and $(NH_4)_2SO_4$ by heating small quantities of the solids in a porcelain dish on the porch.

*Analysis Nos.* 1 *and* 2. Analyze the two "unknowns" for

$H^+$, $Na^+$, $K^+$, $NH_4^+$,
$OH^-$, $Cl^-$, $SO_4^{--}$, $CO_3^{--}$.

In these and all later analyses estimate roughly the concentration of $H^+$ or $OH^-$ in the original solution (see Problem 2, Assignment XIII).

(*Optional work.* Distinguish carbonates and bicarbonates.)

While making these analyses record in your note-book all your experiments and observations, and state clearly the conclusions that you draw. Submit this written report of your analyses to your instructor before proceeding with the next Assignment.

*Problems.* 1. State how you would convert:

(a) Solid sodium carbonate into solid sodium nitrate.
(b) Solid sodium nitrate into solid sodium sulfate.
(c) Solid ammonium chloride into solid sodium chloride.

2. How would you recover the potassium chloride from a mixture of potassium chloride and ammonium chloride.

## ASSIGNMENT XVI.

### Chemistry of Calcium.

In Assignment XVI we shall study the chemistry of metallic calcium and of calcium ion. We shall find that certain compounds of this element differ from the corresponding compounds of sodium, potassium, and ammonium in

* All operations which give rise to noxious fumes must be performed on the porch, not in the laboratory.

that they dissolve to a much smaller extent in water; and we shall study the equilibrium between these solids and their "saturated" solutions. Review the lectures on calcium.)

The *solubility* of a substance in water is the concentration of its *saturated* solution. *Question.* If the solubiltiy of NaCl in water at room temperature is 5.4 mols per liter, how many grams of NaCl are contained in 100 cc. of saturated solution? How could you prove that NaCl (solid) = NaCl (in solution) is a reversible reaction?

*Note.* In future *write equations for all reactions.*

Obtain from the office a piece of metallic calcium. Describe its properties as far as you can observe them by physical examination. In what respects does calcium show the physical properties of a metal?

*Experiment.* Drop the calcium into 20 cc. of water. Stir the mixture or warm gently until the metal has dissolved. Test the solution for $OH^-$. What reaction occurs? The white solid formed, calcium hydroxide, is a strong base but only slightly soluble. *Question.* Name other metals that react readily with water? What reactions occur?

Write the ionic reaction for the dissolving of solid calcium hydroxide to form a saturated solution, and indicate the equilibrium involved. How can the equilibrium be shifted so that more $Ca(OH)_2$ will dissolve? So that less will dissolve?

*Experiment.* Divide the solution of $Ca(OH)_2$ and suspended solid into three parts. Set aside one of these (corked) for future use. To one part add 10 cc. of 1 *N* $NH_4Cl$. Heat the solution and test the odor. To another part add 3 cc. of 6 *N* HCl. What reactions have taken place in these two cases? Note the relation of these reactions to the equilibrium discussed in the preceding paragraph.

To 5 cc. 1 *N* $CaCl_2$ add $Na_2CO_3$ solution *in excess,* heat the mixture to boiling, filter. (The instructor will explain the details of the process of filtration.) The white precipitate is calcium carbonate. Write the simplest ionic equation for its formation. Prove that the *fiiltrate* contains chloride ion.

The fact that the amount of calcium ion in the filtrate must be very small can be deduced from the small solubility of $CaCO_3$ in water, 0.00013 mols per liter.

In any solution saturated with solid calcium carbonate there is an equilibrium between the solid substance and its ions, which may be expressed by the equation

$$CaCO_3 \text{ (solid)} = Ca^{++} + CO_3^{--}.$$

When will a precipitate of calcium carbonate be formed? How is this equilibrium disturbed by the addition of a strong acid? Review or repeat your experiments (Assignment XIV) on the reaction of hydrochloric and acetic acids on $CaCO_3$. Which is the stronger acid, HAc or $H_2CO_3$?

*Experiment.* Pass $CO_2$ gas into a solution of $CaCl_2$. What conclusion do you draw with regard to the concentration of $CO_3^{--}$ in a solution of carbonic acid?

To a solution of $CaCl_2$ add NaOH solution slowly a few drops at a time. Repeat the experiment with $NH_4OH$ solution. What conclusions do you draw with regard to the relative concentrations of $OH^-$ in NaOH and $NH_4OH$ solution?

Now pass $CO_2$ gas into the $CaCl_2$ solution containing $NH_4OH$, and warm the mixture gently.

Filter the third portion of the mixture obtained by the action of calcium on water, and pass a few bubbles of $CO_2$ gas into the filtrate. Under what conditions will $CO_2$ gas form a precipitate of $CaCO_3$ in a solution containing $Ca^{++}$? Which is the less soluble substance, $CaCO_3$ or $Ca(OH)_2$?

Test the action of excess $CO_2$ on the same mixture by passing $CO_2$ gas into a small quantity of the mixture for some time. The reaction involves the formation of bicarbonate ion, $HCO_3^-$, $H_2CO_3 + CaCO_3$ (solid) $= Ca^{++} + 2HCO_3^-$. There is an equilibrium. Point out how the reverse reaction can be made to take place. (*Optional Question.* Point out how these results are related to the results of the optional experiments at the end of Assignment XIV.)

*Experiment.* Determine whether calcium salts give a characteristic flame test. Can you distinguish the flame with a calcium salt from that with sodium or potassium salts?

*Experiment.* To 10 cc. normal $CaCl_2$ solution add 2 cc. 6 normal $H_2SO_4$. If no precipitate appears at once, heat the solution gently, and let it stand. Filter. Test a portion of the filtrate for $Ca^{++}$ by adding $NH_4OH$ until the solution is no longer acid, and then $(NH_4)_2CO_3$ solution, and warm the mixture. Test another portion for $SO_4$ by adding $BaCl_2$ solution. What conclusion do you draw with regard to the solubility of $CaSO_4$? Which is the less soluble, (1) $CaSO_4$ or $CaCO_3$, (2) $CaSO_4$ or $BaSO_4$?

Predict what will take place when solid $CaSO_4$ is heated with excess $Na_2CO_3$ solution? *Experiment.* Test your prediction by boiling some solid $CaSO_4$ with normal $Na_2CO_3$ solution. Test the filtrate for $SO_4^{--}$. Wash the precipitate with water, and test it for carbonate.

Test whether the reverse reaction will take place by heating solid $CaCO_3$ with sodium sulfate solution, filtering and testing the precipitate and filtrate.

*Problems.* 1. Arrange the compounds of calcium according to their solubilities in water, distinguishing readily soluble, moderately soluble, and difficultly soluble substances. Point out the compounds which are much more soluble in dilute hydrochloric or nitric acids than in water.

2. Can the following substances be present at high concentrations in the same solution? If not, what is formed?

(a) $H^+$ and $NO_3^-$
(b) $H^+$ and $OH^-$
(c) $H^+$ and $SO_4^{--}$
(d) $H^+$ and $CO_3^{--}$
(e) $H^+$ and $HCO_3^-$
(f) $Ca^{++}$ and $CO_3^{--}$
(g) $Ag^+$ and $Cl^-$
(h) $H_2CO_3$ and $CO_3^{--}$

## ASSIGNMENT XVII.

### Action of Acids on Metals. Soluble Salts of Zinc, Copper and Silver.

Describe the physical properties of zinc, copper and silver, noting any characteristic property of each metal.

*Zinc and Acids.* Review your experiments on the action of acids on zinc. Write the ionic equations for the reaction between zinc and solutions of hydrochloric and sulfuric acids. What is the color of $Zn^{++}$? Is it correct to say that an atom of the metal has *combined* with $2Cl^-$ or with $SO_4^{--}$? How can solid zinc chloride and solid zinc sulfate be prepared from these solutions?

From an examination of the ionic equation which you have just written state how you would expect the *speed of the reaction* to alter with the concentration of $H^+$. *Experiment.* Test your answer by treating small pieces of zinc with (a) a small volume of 6 normal HCl, (b) the same amount of HCl in a large volume of water, and (c) 6 normal acetic acid solution. In the same experiments determine how the speed of the reaction is altered by an increase of temperature.

When Zn reacts with 6 normal $HNO_3$ the principal reaction, written in its simplest form, is

$$3Zn(\text{solid}) + 2NO_3^- + 8H^+ = 3Zn^{++} + 2NO(\text{gas}) + 4H_2O$$

NO gas is colorless. What is the reaction between NO and oxygen of the air? Repeat the experiment with Zn and $HNO_3$ solution, if necessary. Place the metal and acid in a small beaker and cover it with a watch glass.

*Copper and Acids. Experiment.* Try the action of 6 normal HCl and of 6 normal $H_2SO_4$ on metallic copper. After a rew minutes remove the pieces of metal, wash them with water, and note if the appearance has changed. Then test the action of fresh solutions of the acids on the clean metal. Is there any evidence of chemical action?

Try the action of 6 normal $HNO_3$ on metallic copper. Save the solution. What is the color of the copper ion (cupric ion), $Cu^{++}$? The reaction is similar to that between Zn and nitric acid solution. Write the equation.

*Silver and Acids. Experiment.* Try the action of 6 normal HCl, 6 normal $H_2SO_4$, and 6 normal $HNO_3$ on silver. Compare with the corresponding actions in the case of zinc and copper. Save any solution you obtain. What is the color of silver ion, $Ag^+$? Write the equation for the reaction with nitric acid solution, noting that the change from 1 atom Zn to $Zn^{++}$ corresponds to the change from 2 atoms Ag to $2Ag^+$.

A summary of the results of these experiments is asked for in Problem 1 below.

*Solubility of Nitrates. Chlorides and Sulfates of Metals.* What conclusion can you draw from the above experiments with regard to the solubility of the nitrates of zinc, copper and silver. State how you could prepare the solid nitrates from your solutions. Give the formulas. Note that the nitrates of all metals are soluble in water.

*Experiment.* To a small portion of your solution containing $Ag^+$ add a few drops HCl solution; to another portion add a few drops $H_2SO_4$ solution. Repeat these experiments with your solution containing $Cu^{++}$. What conclusions can you draw with regard to the solubility of AgCl, $Ag_2SO_4$, $CuCl_2$ and $CuSO_4$ in water? Note that nearly all the chlorides and sulfates of metals are soluble in water. There are only a few exceptions in each case. Give an example of a difficultly soluble sulfate.

*Preparation of Sulfates from Nitrates and Chlorides.* Suggest a method of preparing solid copper sulfate from copper nitrate based on the difference in volatility of $HNO_3$ and $H_2SO_4$. Try your method with your solution which contains $Cu^{++}$, $NO_3^-$ and $H^+$ (which is usually spoken of as a solution of copper nitrate and nitric acid). Collect some crystals of copper sulfate by evaporating the final solution to a very small volume, and letting it cool slowly. Wash the crystals with a very little water and save them.

Suggest a similar method of preparing solid zinc sulfate from a solution of zinc chloride. How would you test whether the final product is free from chloride?

The problem of preparing a soluble chloride or nitrate from a sulfate will be considered later. Suggest a method now if you can.

*Conversion of Soluble Chlorides into Nitrates, and Nitrates into Chlorides. Experiment.* Mix 2 cc. concentrated $HNO_3$ solution and 5 cc. concentrated HCl solution, and let the mixture stand. Is there any evidence of chemical action? The same reaction takes place when a dilute solution of the two acids is evaporated to a small volume. Do not attempt to write the equation. Both acids are destroyed, and this reaction may be used to remove completely chloride or nitrate from a solution by adding a concentrated solution of the other acid in large excess and evaporating almost to dryness.

*Experiment.* Dissolve about 0.5 g. zinc in hydrochloric acid, evaporate the solution to a small volume, add some concentrated $HNO_3$ solution, and evaporate the mixture almost to dryness on the porch. Test the residue for

chloride, and repeat the treatment with concentrated nitric acid, if necessary.

How would you reconvert the zinc nitrate into zinc chloride?

*Water of Crystallization.* Note the appearance of the copper sulfate crystals you have prepared. Examine also the large crystals in the bottle of copper sulfate in the laboratory. The formula is $CuSO_4 \cdot 5H_2O$, and the water present in the solid is called "water of crystallization". Many other salts, such as crystalline zinc sulfate, also contain water of crystallization.

*Experiment.* Heat a small quantity of $CuSO_4 \cdot 5H_2O$ in a porcelain evaporating dish, and note the change in its appearance. The residue is *anhydrous* copper sulfate, $CuSO_4$. Write the equation for the reaction. When the dish is cool add a few drops of water. What reaction will take place when water vapor is passed over anhydrous $CuSO_4$ at a low temperature? Under what conditions will there be an equilibrium?

Give another example of an equilibrium involving two solids and a gas. How does the pressure of the gas at equilibrium vary with the temperature?

*Problems.* 1. Summarize what you know about the action of acids on Na, K, Ca, Zn, Cu, Ag and any other metals discussed in the lectures by dividing the metals into the three following classes:

I. Those which react readily with water. Hydrogen is evolved.

II. Those which react readily with HCl or $H_2SO_4$ solution, but not with water. Hydrogen is evolved.

III. Those which dissolve readily in $HNO_3$, but not in HCl, $H_2SO_4$ or water. $H_2$ is not evolved.

Write the equation for the action of HCl or $H_2SO_4$ on metallic sodium.

2. How would you prepare solid silver sulfate from metallic silver? What weight of the sulfate could be obtained from 1 gram of silver?

## ASSIGNMENTS XVIII TO XX.

### Chemistry of Cupric Ion, Silver Ion, and Zinc Ion.

In the next three Assignments we shall study the chemistry of the ions $Cu^{++}$, $Ag^{+}$, and $Zn^{++}$,—especially the preparation of difficultly soluble compounds, methods of dissolving them, and the equilibria involved.

While doing this work collect the information necessary to complete the following table, performing additional experiments when necessary. This table is intended to summarize the action of various reagents on the different positive ions. Leave a blank when there is no action. Mark the colors of the precipitates, and add notes in the table, or below the table, to show methods of dissolving them. Be sure that you can write the equation for each reaction. The information thus summarized will be used in Assignment XXI in planning methods of qualitative analysis.

| Reagents | $Ca^{++}$ | $Cu^{++}$ | $Ag^{+}$ | $Zn^{++}$ |
|---|---|---|---|---|
| $Cl^-$ | — | — | AgCl, white soluble in ? | — |
| $OH^-$ | $Ca(OH)_2$, | | | |
| $OH^-$ in excess | moderately soluble. | | | |
| $NH_4OH$ | — | | | |
| $NH_4OH$ in excess | — | | | |
| $CO_3^{--}$ | $CaCO_3$ soluble in acids. | | | |
| $H_2S$ in acid solution | ? | | | |
| $S^{--}$ in alkaline solution | ? | | | |
| Ferrocyanide ion $Fe(CN)_6^{----}$ | ? | | | |

## ASSIGNMENT XVIII.

### Hydroxides and Oxides.

*Experiment.* To solutions containing $Cu^{++}$, $Ag^{+}$ and $Zn^{++}$, in separate test tubes, add a few drops NaOH solution. In the experiments with copper and silver continue to add NaOH solution until the mixture, after shaking, reacts strongly alkaline to litmus. Collect the precipitates on filters. The precipitates are the hydroxides of copper and zinc and the oxide of silver, $Ag_2O$. Write equations to show the formation of the solids from the ions. There is an equilibrium in each case. How will each equilibrium be affected by the addition of a strong acid?

Test the action of nitric acid on the precipitates just obtained. Compare your equations with that for the action of a strong acid on solid calcium hydroxide.

To solutions containing $Cu^{++}$, $Ag^{+}$, and $Zn^{++}$, in separate tubes, add a few drops $NH_4OH$ solution. Do not add excess.

*Experiment.* Collect some zinc hydroxide on a filter. Treat a portion with hydrochloric acid, and another portion with sodium hydroxide solution. All hydroxides and oxides of metals react with acids to from water (cf. neutralization), and the reaction usually takes place rapidly. Some of them, as in the case of zinc, also react with strong bases to form water, and the reaction again corresponds to neutralization. Compare

$$H_2ZnO_2(\text{solid}) + 2OH^- = 2H_2O + ZnO_2^{--}$$

and

$$H_2CO_3 + 2OH^- = 2H_2O + CO_3^{--}.$$

$ZnO_2^{--}$ is zincate ion, and $Na_2ZnO_2$ is sodium zincate. What reaction takes place when $Zn^{++}$ is treated with excess $OH^-$?

State if any other hydroxide of a metal which reacts with a strong base in a similar manner has been discussed in the lectures, and write the equation.

*Experiment.* Collect some $Cu(OH)_2$ on a filter, wash it once with water, and heat some of it in a porcelain dish. Cupric oxide has been formed. In order to determine if this is a reversible reaction, allow the dish to cool and add water. Also heat a mixture of cupric hydroxide and water to boiling. What reaction would take place if NaOH solution were added to a solution of copper nitrate at 100°?

The hydroxides of all metals except the alkali metals are decomposed into the oxide and water vapor when the dry solids are heated strongly. In most cases the oxides will remain unchanged in contact with water, ZnO is an example. In some cases, however, the reaction is reversible. What happens when water is added to calcium oxide? Under what conditions will there be an equilibrium?

The oxides of the alkali metals, as $Na_2O$, react violently with water Write the equation. Solid NaOH melts without decomposition.

*Problems.* 1. Write equations for the action of HCl solution on calcium oxide, on ferrous and ferric oxides (FeO and $Fe_2O_3$), and on ferrous and ferric hydroxides.

2. How would you prepare solid copper nitrate (a) from cupric hydroxide, (b) from cupric sulfate?

3. Give three examples, as widely different as possible, in which there is an equilibrium involving two solids and a gas. In each case state how the pressure of the gas at equilibrium alters with the temperature.

## ASSIGNMENT XIX.

### Complex Ions Containing Ammonia.

The ions of certain metals have the power of forming compounds with ammonia, $NH_3$. The ammonia is supplied by adding $NH_4OH$ solution. There is an equilibrium between the ion of the metal, $NH_3$ or $NH_4OH$ and the complex ion; and when $NH_4OH$ is present in excess the concentration of the ion of the metal is often very small. Some examples will be studied in Assignment XIX.

*Experiment.* Collect some copper hydroxide on a filter, wash it with a little water, and treat it with 6 normal $NH_4OH$ solution. Give reasons why the reaction cannot be similar to that of $OH^-$ on zinc hydroxide. The deep blue substance is $Cu(NH_3)_4^{++}$. How is the equilibrium between solid $Cu(OH)_2$ and its ions affected by the addition of $NH_4OH$? Which solution has the smaller concentration of $Cu^{++}$, a saturated solution of $Cu(OH)_2$ or the solution containing the complex ion?

From a consideration of the equilibrium

$$Cu^{++} + 4NH_4OH = Cu(NH_3)_4^{++} + 4H_2O$$

predict what will happen when the solution is acidified with nitric acid. Test your conclusions.

Silver and zinc also form complex ions with amonia, $Ag(NH_3)_2^+$ and $Zn(NH_3)_4^{++}$.

*Experiment.* Prepare some silver oxide and zinc hydroxide, and test the action of excess $NH_4OH$ solution.

Predict what will be the effect of treating a silver chloride precipitate with $NH_4OH$ solution. Test your conclusions by an experiment. Acidify the final solution with nitric acid.

In addition to the alkali metals and alkaline earth metals there are many metals which do not form complex ions with amonia. Give examples if you can.

*Problems.* 1. Write equations for the reaction between $Cu^{++}$ and $NH_4OH$ (1) when a few drops $NH_4OH$ solution are added, and (2) when excess $NH_4OH$ is added.

2. Give at least one example of the formation of a complex ion of a metal, other than an ammonia complex.

## ASSIGNMENT XX.

### Carbonates, Sulfides, Ferrocyanides.

*Experiment.* Try the action of $Na_2CO_3$ solution on $Cu^{++}$, on $Ag^+$, and on $Zn^{++}$. In each case collect the precipitate on a filter, wash it with water, and test a portion for carbonate. Predict the action of nitric acid solution and of ammonium hydroxide solution on these precipitates, and test your prediction by experiments with $HNO_3$ and $NH_4OH$ solutions.

Predict the action of $NH_4OH$ solution on calcium carbonate, and test your answer by an experiment.

*Experiment.* To solutions containing small amounts of $Cu^{++}$, $Ag^+$, and $Zn^{++}$, in separate experiments, add 1 cc. 6 normal $H_2SO_4$; dilute each solution to about 20 cc., and pass $H_2S$ gas* into it until the liquid is saturated with the gas. To determine this, close the end of the test tube or flask, shake thoroughly, and test the odor cautiously. In the experiment with $Zn^{++}$ and $H_2S$ add 5 cc. 2 normal sodium acetate solution, and again saturate with $H_2S$ gas. Collect the precipitates on separate filters.

* Caution. $H_2S$ is poisonous. Work with it on porch, and do not breathe it.

Predict the action of 0.3 normal $H_2SO_4$ on each precipitate. Treat portions of each precipitate with 0.3 normal $H_2SO_4$ and with 2 normal $H_2SO_4$. Is zinc sulfide more or less soluble than copper sulfide? Give your reasoning.

To solutions containing $Cu(NH_3)_4^{++}$, $Ag(NH_3)_2^{+}$, and $Zn(NH_3)_4^{++}$, in separate experiments, add $(NH_4)_2S$ solution. Repeat the experiments, using $H_2S$ gas instead of $(NH_4)_2S$ solution. State in each case which has the smaller concentration of the ion of the metal, a solution containing the complex ion, or a solution saturated with the sulfide. State also which is the less soluble, $Cu(OH)_2$ or $CuS$, $Ag_2O$ or $Ag_2S$, $Zn(OH)_2$ or $ZnS$.

Predict the action of $H_2S$ on mixtures of copper carbonate and water, silver carbonate and water, and zinc carbonate and water. Test your answers by experiments. State in each case which is the less soluble, the carbonate or the sulfide.

Test the action of $H_2S$ on solutions of nitric acid of different concentrations, 0.1 normal, 2.0 normal, and 6 normal. Saturate each solution with $H_2S$ gas, and heat the mixture almost to boiling. The principal reaction is

$$3H_2S+2NO_3^-+2H^+=3S(\text{solid})+2NO+4H_2O.$$

Compare this equation with that for the action of nitric acid on metallic Zn or Cu.

Collect some CuS on a filter, transfer it to a casserole, add 2 normal $HNO_3$ and boil the mixture. Filter, and test the filtrate with excess $NH_4OH$. The residue collected on the filter is sulfur; the dark color is due to a little CuS enclosed in the sulphur. Complete the equation

$$3CuS(\text{solid})+2NO_3^-=3S(\text{solid})+2NO.$$

Repeat the experiment, using silver sulfide instead of copper sulfide.

*Experiment.* To very dilute solutions containing $Cu^{++}$, $Ag^{+}$, and $Zn^{++}$, respectively, add a few drops potassium ferrocyanide solution, $K_4Fe(CN)_6$. Repeat these experiments in the presence of (1) a little acetic acid, (2) a little hydrochloric acid. A ferrocyanide frequently furnishes a *characteristic* final test for an ion, on account of the color; but ferrocyanides are seldom used in making separations.

*Experiment.* Determine which is the most delicate test for copper by preparing very dilute solutions of $Cu^{++}$, e.g. $N/1000$, N/10,000, etc., and testing separate 10 cc. portions with $NH_4OH$, with $H_2S$ and with $K_4Fe\ (CN)_6$.

*Problems.* 1. Hydrogen sulfide in solution is a weak dibasic acid which, like $H_2CO_3$, ionizes in two stages. Review the neutralization reactions of carbonic acid (Assignment XIV), and write equations for the neutralization of (1) $H_2S$ with one mol $OH^-$, (2) $H_2S$ with excess $OH^-$, and (3) $HS^-$ with $OH^-$. Write the equation for the hydrolysis of sulfide ion, $S^{--}$.

2. Is it correct to state that *all* difficulty soluble salts of a weak acid dissolve when a solution of any strong acid is added? Explain, giving examples.

3. What is a "basic salt?" Give an example of a basic carbonate.

Note. Leave your two clean sample bottles at the office, labelled with your name and desk number, and marked No. 3 and No. 4, in order that two unknowns may be ready for you at the next laboratory period.

## ASSIGNMENT XXI.

### Review. Qualitative Analysis.

Test what you know of the chemistry of cupric copper, silver and zinc, as studied in the preceding Assignments, by preparing from memory a summary for each metal showing

I the formulas of the ions (including the complex ions);

II the readily soluble and moderately soluble compounds;

III the difficulty soluble compounds noting which is the least soluble.

Check each item by reference to your laboratory notes, and correct your mistakes.

Complete the table given just before Assignment XVIII, and use this table in planning how to analyze the various solutions of salts referred to below. Perform additional experiments whenever you are not certain that your methods are satisfactory.

Give a method of detecting silver in a solution which may contain $Cu^{++}$, $Ca^{++}$ and $Na^{+}$. How could you separate silver from a solution containing any of these ions?

Give two methods for each of the following separations: (a) $Cu^{++}$ from $Zn^{++}$, (b) $Cu^{++}$ from $Ca^{++}$. (c) $Cu^{++}$ from $Na^{+}$, (d) $Zn^{++}$ from $Ca^{++}$, (e) $Zn^{++}$ from $Na^{+}$.

A solution contains $Ag^{+}$, $Cu^{++}$, $Zn^{++}$, $Ca^{++}$, and $Na^{+}$. Devise a series of operations which would enable you to prepare a compound of each element from a single portion of the solution. *Experiment.* Test your method with a solution containing all of these ions, and apply additional tests, when necessary, to prove that each of these ions was present in the original solution. Such a series of operations is a scheme of qualitative analysis for these ions.

A knowledge of the positive ions present in a solution often enables the conclusion to be drawn that certain negative ions cannot be present in appreciable amounts. What negative ions need not be tested for when the following are present at moderate concentrations? (a) $H^{+}$, (b) $Ca^{++}$, (c) $Zn^{++}$, (d) $Cu^{++}$, (e) $Ag^{+}$.

*Experiment. Test for nitrate ion.* $NO_3^-$ To about 2 cc. of the solution to be tested add excess ferrous ammonium sulfate ($FeSO_4:(NH_4)_2SO_4$) solution, or add the solid salt, filter if there is a precipitate, hold the test tube in a slanting position and pour carefully down the side (from a small beaker) 3 to 5 cc. concentrated sulfuric acid. The concentrated acid sinks to the bottom of the test tube and a dark brown ring forms on its surface when nitrate is present. This brown substance decomposes when the solution is heated.

*Analysis* 3 *and* 4. Test for

$H^{+}$, $Ag^{+}$, $Cu^{++}$, $Zn^{++}$, $Ca^{++}$, $Na^{+}$, $K^{+}$, $NH_4^{+}$,
$OH^{-}$, $Cl^{-}$, $NO_3^{-}$, $SO_4^{--}$, $CO_3^{--}$, $S^{--}$.

When an ion is found to be present, try to decide whether it is present in a large amount, in a small amount, or as a mere trace.

In the second term A. A. Noyes' "Qualitative Analysis," *new edition,* 1914, will be used; it is for sale at the Co-operative Store, price $1.50. The new edition is the same as that used in 1914-15, but differs greatly from that used in 1913-14.